

TITLE: ATOMIC-LEVEL IMAGING OF CO₂ DISPOSAL AS A CARBONATE MINERAL: OPTIMIZING REACTION PROCESS DESIGN

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ABSTRACT

OBJECTIVE

The goal of this project is to develop an atomic level understanding of the mechanisms that govern the kinetics of the complex Mg(OH)₂ carbonation process to facilitate engineering of improved carbonation materials and processes for carbon dioxide disposal. The primary tool for this project is environmental-cell (E-cell) dynamic high-resolution transmission electron microscopy (DHRTEM). Other techniques are incorporated to optimally elucidate the overall reaction process (e.g., *in-situ* vs. *ex-situ* studies and studies based on reactant particle and crystalline grain size). As the overall carbonation process involves dehydroxylation, carbonation and the potential competition between them, developing an atomic-level understanding of the dehydroxylation process is first targeted to provide a foundation from which to explore the overall carbonation process. Process mechanisms are targeted for exploration as a function of potential feedstock material characteristics, which may be incorporated to enhance carbonation: (i) high purity Mg(OH)₂ single crystal fragments to elucidate basic reaction processes for highly crystalline material, (ii) Mg(OH)₂ materials containing crystalline defects to probe the effect of grain boundaries, crystallinity, etc. on reaction processes, and (iii) Mg(OH)₂ materials containing known impurities to investigate the effects of impurities (e.g., Ca) on dehydroxylation/carbonation processes:

ACCOMPLISHMENTS TO DATE

During the initial project period, the materials and operational foundation for the project have been established, including (i) development of the CO₂/H₂O gas mixing system for the E-cell DHRTEM studies, (ii) evaluation and characterization (morphological, structural and elemental) of a number of potential feedstock materials for reaction process studies, and (iii) development of appropriate sample preparation techniques for the E-cell DHRTEM studies.

DHRTEM observations of the *in situ* Mg(OH)₂ dehydroxylation process together with advanced computational modeling indicate dehydroxylation proceeds by a lamellar nucleation and growth process. Lamellar oxide nuclei form via the dehydration of single double hydroxide layers or layer regions (e.g., $\cdots\text{OH/Mg/OH/OH/Mg/OH}\cdots \rightarrow \cdots\text{OH/Mg/O/Mg/OH}\cdots + \text{H}_2\text{O}$). Growth occurs by the formation of additional nearby oxide lamella, creating lamellar oxyhydroxide regions, which can grow both parallel and perpendicular to the Mg(OH)₂ lamella in the host Mg(OH)₂ matrix. The oxide lamella have a substantial theoretical in-plane close packing mismatch with the adjacent hydroxide lamella (the in-plane close-packing Mg-Mg distance of 2.98Å for ideal MgO lamella is 5% smaller than that observed for the Mg(OH)₂ lamella: 3.15Å). Electron diffraction of the *in-situ* dehydroxylation process supports the general applicability of a novel two-dimensional variant of Vegard's law in the oxyhydroxide regions, with the regions exhibiting intermediate lamellar Mg-Mg packing distances. The associated stress within these regions is believed to strongly contribute to crystallite cracking during dehydroxylation and the (111) to (100) surface reconstruction of the resulting MgO. Such a lamellar nucleation and growth process can take on homogeneous or biphasic character via slow nucleation/rapid growth and rapid nucleation/slow growth, respectively. This may have important implications for optimizing Mg(OH)₂ carbonation, as controlled dehydroxylation during carbonation may have the potential to create intermediate interfaces with large areas to enhance carbonation reactivity. A range of dehydroxylation control may be possible, as initial carbonation studies suggest dehydroxylation may occur in advance of, as well as during, carbonation.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS

Fossil fuels, especially coal, can support the energy demands of the world for centuries to come, if the environmental problems associated with CO₂ emissions can be overcome. Mineralization of stationary-source CO₂ emissions as carbonates can provide safe capture and long-term sequestration. Mg(OH)₂ carbonation is a leading carbonate process candidate, generating the stable, naturally-occurring mineral magnesite (MgCO₃). Optimizing the carbonation reaction rate and its degree of completion are key to process cost and viability. This project focuses on investigating the process reaction mechanisms at the atomic level to provide the mechanistic understanding to facilitate the engineering of improved carbonation materials and processes for carbon dioxide disposal.

PLANS FOR THE COMING YEAR

The primary focus will be to (i) continue the studies of $\text{Mg}(\text{OH})_2$ single crystal fragments and (ii) extend these studies to $\text{Mg}(\text{OH})_2$ feedstock materials with variable levels of crystallinity, including defect structures, to probe their role in dehydration/carbonation mechanisms and reactivity.

ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Journal Articles (peer reviewed)

- McKelvy, M.J., Sharma, R., Chizmeshya, A.V.G., Streib, K., Carpenter, R.W. “ $\text{Mg}(\text{OH})_2$ Dehydroxylation: A Lamellar Nucleation and Growth Process,” to be submitted shortly.
- Chizmeshya, A.V.G., McKelvy, M.J., Sharma, R., Carpenter, R.W. “ $\text{Mg}(\text{OH})_2$ Dehydroxylation: A Non-Empirical Density Function Approach,” to be submitted shortly.

Conference Presentations

- McKelvy, M.J., Carpenter, R.W., Sharma, R. “Atomic-Level Imaging of CO_2 Disposal as a Carbonate Mineral: Optimizing Reaction Process Design,” the *Carbon Dioxide Mineral Sequestration Forum*, Los Alamos, New Mexico, 1998.
- McKelvy, M.J., Carpenter, R.W., Sharma, R., Streib, K. “Atomic-Level Imaging of CO_2 Disposal as a Carbonate Mineral: Optimizing $\text{Mg}(\text{OH})_2$ Carbonation,” *Carbon Dioxide Mineral Sequestration Working Group Meeting*, Albany, Oregon, 1998.
- McKelvy, Michael J., Sharma, Renu, Chizmeshya, Andrew V.G., Carpenter, Ray W., Streib, Ken “ $\text{Mg}(\text{OH})_2$ Dehydroxylation: A Lamellar Nucleation and Growth Process,” *University Coal Research Contractors Review Meeting*, Pittsburgh, Pennsylvania, 1999 (submitted for presentation).

Students Supported under this Grant

- Kenneth Streib, graduate (Ph.D.) student in the Science and Engineering of Materials Ph.D. Program, Arizona State University
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